

Requested Patent: GB1003147A

Title: PROCESS FOR NAPHTHA REFORMING ;

Abstracted Patent: US3262886 ;

Publication Date: 1966-07-26 ;

Inventor(s): BERNAS ARNOLD R;; RUSSELL JAMES GEORGE ;

Applicant(s): CHEMICAL CONSTRUCTION CORP ;

Application Number: US19610160749 19611220 ;

Priority Number(s): US19610160749 19611220 ;

IPC Classification: ;

Equivalents: BE624622, DE1442991, NL285248 ;

ABSTRACT:

# PATENT SPECIFICATION

1,003,147

DRAWINGS ATTACHED.

1,003,147



Date of Application and filing Complete Specification:  
Oct. 22, 1962. No. 39824/62.

Application made in United States of America (No. 160,749)  
on Dec. 20, 1961.

Complete Specification Published: Sept. 2, 1965.

© Crown Copyright 1965.

Index at Acceptance:—C1 A(K5, K6).

Int. Cl.:—C 01 b.

## COMPLETE SPECIFICATION.

### Naphtha Reforming Process.

We, CHEMICAL CONSTRUCTION CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 320 Park Avenue, New York 22, State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for forming a hydrogen-nitrogen gas stream, for instance an ammonia synthesis gas. A new approach to catalytic steam-reforming of naphtha has been developed, in which naphtha is completely converted to a synthesis gas stream by externally fired catalytic steam reformer, without concomitant accumulation of free carbon. The formation of lower hydrocarbons by thermal cracking is also controlled and becomes a transient phenomenon, and thus the final process gas stream contains only a negligible proportion of unreacted lower hydrocarbons.

Naphtha is a relatively volatile petroleum refining product or intermediate, which is generally defined in terms of boiling range. Thus, according to a crude oil survey in Industrial and Engineering Chemistry 44 #11 (Nov. 1952) p. 2578, naphtha is defined as follows: "Naphtha content (of crude oil) is the total distillate recovered in the U.S. Bureau of Mines routine analysis at a vapor temperature of 392°F". A more detailed definition of naphtha appears in "Petroleum Refining With Chemicals" by Kalichevsky & Kobe (1956). A discussion of naphtha on p. 21—23 of this text indicates that different naphthas may have boiling ranges from a low point of 122°F to a maximum of 400°F. Thus "naphtha" is defined as a general term which is applied to fractions boiling in the gasoline of low kerosene range. In general

then, naphtha is a low-boiling and readily volatilized liquid hydrocarbon cut, derived from crude oil distillation in petroleum refining. This materials consists mostly of straight chain paraffins in the C-5 to C-9 range, however, up to about 30% naphthenes together with up to 10% aromatics and unsaturated hydrocarbons may also be present. In addition, naphtha also generally contains a significant proportion of sulfur in the form of COS and mercaptans.

Naphtha may be utilized in a variety of ways. Thus, crude naphtha may be further refined and upgraded to yield a variety of finished petroleum solvents. In many refineries, naphtha is "reformed" in the petroleum sense of the term. In this case, the crude naphtha is cracked, and hydrocarbon molecules are re-assembled in the presence of platinum or other suitable catalyst, so as to yield a substantial proportion of branched chain or aromatics molecules. This material is then blended with other refinery cuts for gasoline usage. In the terminology of the present invention, the word "reforming" has an entirely different meaning, and applies to conversion of a hydrocarbon to a gas stream substantially comprising simple molecules, not larger hydrocarbon molecules, for instance, hydrogen, carbon monoxide and carbon dioxide.

Finally, naphtha may also be utilized as a hydrocarbon raw material for the manufacture of hydrogen or ammonia synthesis gas. There are two general approaches to the conversion of the various types of hydrocarbons to synthesis gas, namely, steam reforming and partial oxidation. In steam reforming, a normally gaseous hydrocarbon such as methane is mixed with steam, and the mixture is then passed through an externally heated bed of nickel-containing reform catalyst. An endothermic reaction takes

[Price 4s. 6d.]

place between the hydrocarbon and steam, resulting in the formation of a "synthesis gas" product stream containing principally hydrogen, carbon monoxide and carbon dioxide.

In the case of partial oxidation, a hydrocarbon raw material is reacted with oxygen or oxygen-enriched air at a highly elevated temperature. The product stream is then quenched, to yield a crude synthesis gas stream. A catalyst is not employed in conventional partial oxidation practice, since essentially complete reaction of the hydrocarbon is readily accomplished at the high temperature levels generated in this process. In addition, a variety of hydrocarbons may be employed in partial oxidation, including liquid or even powdered solid hydrocarbons as well as gases.

As is well known in the art, catalytic steam reforming is generally limited to the usage of gaseous hydrocarbons, due to such problems as partial conversion and carbon deposition, when vaporized liquid hydrocarbons are employed. One approach to the steam reforming of higher hydrocarbons such as naphtha is described in U. S. Patent No. 2,940,840. In this process, the formation of free carbon in the catalyst bed is purposely brought about by overloading the catalyst. Although this process is cyclic and requires a regeneration period during which the deposited carbon is oxidized for removal, it is claimed that the overall process efficiency is better than in prior practice. Another recent approach to the problem is described in U. S. Patent 2,943,062. A partial oxidation effect is obtained in a catalytic process by adding oxygen to a stream of hydrocarbon vapor or partially reformed gas, immediately before the stream is passed through a catalyst bed. The bed is not externally heated, instead the process is carried out in a refractory-lined chamber as in conventional partial oxidation. It will be evident that this procedure is subject to the principal economic drawback of all partial oxidation processes, namely, that a plant for separating oxygen from air is required.

In the present invention, naphtha is catalytically steam-reformed to produce an ammonia synthesis gas. Thus, a limited amount of process air is employed in the present invention to assist in the gasification of the naphtha prior to catalytic reform, as well as to provide the nitrogen gas component for subsequent ammonia synthesis. By "gasification" herein is meant the decomposition or reforming of the hydrocarbon or naphtha to the product gases. The process of the present invention depends on a unique balance of reaction conditions to achieve the catalytic steam reforming of naphtha, since this is accomplished without accumulated deposition of free carbon. In addition, no

significant amount of unreacted hydrocarbon is present in the final synthesis gas. The process is carried out in two stages, a gasification-conditioning stage and a catalytic steam reform stage. These stages of the process are distinctly co-acting and dependent, in that it has been found that the conditioning stage must be of short duration in order to prevent the reactants from reaching equilibrium with resultant deposition of free carbon in the catalyst bed. It has also been found that the reactants must be preheated in order to provide a minimum temperature level in the conditioning stage. Thus, in the present invention, process streams of naphtha, steam and air are preheated and mixed. A partial reaction ensues, and the mixed process stream, now containing a variety of intermediate components but not in final reaction equilibrium, is passed through an externally heated bed of reform catalyst. A final process stream is produced by steam reforming of residual naphtha and intermediate lower hydrocarbons. This final process stream consists of a synthesis gas containing principally hydrogen, nitrogen, carbon monoxide and carbon dioxide. The stream is essentially free of unreacted hydrocarbons or solid particulate carbon.

According to the present invention therefore there is provided a process for forming a hydrogen-nitrogen gas stream which comprises vaporizing and preheating naphtha to a temperature up to 1000°F., superheating steam, and preheating air, combining said streams of naphtha, steam and air to form a mixed gaseous stream at a temperature of at least 1000°F., reacting said mixture for an interval less than 1.0 seconds in which said naphtha is simultaneously oxidized, cracked and partially reformed without accumulated deposition of free carbon, and catalytically reforming the resulting gas mixture in contact with a reform catalyst at an equivalent linear velocity of at least 5 ft./sec., said catalyst being externally heated to maintain a reaction temperature of at least 1400°F., whereby a final reformed gas mixture substantially free of hydrocarbons and comprising hydrogen, nitrogen, steam, carbon monoxide and carbon dioxide is produced, without accumulated deposition of free carbon.

Preferably the conditions are adjusted so that the naphtha is vaporized and preheated to a temperature of 400°F. to 800°F., the mixed gaseous stream of naphtha, steam and air is at a temperature of 1400°F. to 1700°F. and pressure in the range of 100 to 300 psig, and said mixed gaseous stream has a steam/carbon molar ratio between 5 to 1 and 7 to 1, and is reacted for a time interval from 0.05 to 0.33 seconds, and the resulting gas mixture catalytically reformed with the catalyst maintained at a reaction temperature of at least 1600°F., said gas mixture having a linear

gas velocity in the range of 10 to 30 ft./sec. during said catalytic reform.

The mixed gas stream produced after the first reaction time interval is preferably divided into a plurality of partial streams and said partial streams are passed into contact with said catalyst in a catalyst bed at a plurality of spaced intervals, wherein the resulting catalytic reforming reaction takes place at a substantially uniform rate throughout said catalyst bed and localized temperature depression is prevented. Said catalyst is preferably disposed in a bed having progressively increasing catalytic activity per unit volume of bed in the downstream direction of gas flow. Furthermore the bed is preferably vertically oriented and said mixed gas stream is passed downwardly through said bed.

The process of the present invention possesses several significant advantages. A primary advantage is that naphtha is catalytically steam reformed to ammonia synthesis gas, without the concomitant accumulation of free carbon or tars, and without the production of lower hydrocarbons as a significant component of the final process stream. Thus, no recycle or side stream disposal is required. The process is continuous rather than cyclic or intermittent. In addition, one major economic cost in partial oxidation processes, namely a plant for separating oxygen from air or other source of oxygen, is not required in the process of the present invention. Finally, conventional steam reformer apparatus rather than a special or costly apparatus may be employed in the catalytic reforming stage of the present invention.

The invention will now be described with reference to the accompanying drawing which is a schematic diagram of the method of the invention. Stream 1 is a liquid naphtha, derived from petroleum refining or other types of crude oil processing. Thus, as described supra, stream 1 consists principally of straight chain paraffinic hydrocarbons in the C-5 to C-9 range, together with naphthenes as well as minor amounts of aromatic and sulfur compounds. The liquid stream 1 is vaporized and preheated in heater 2, to form naphtha vapor stream 3. Vapor stream 3 may be produced at any suitable temperature, ranging from the boiling point of naphtha up to 1000°F. Above this temperature level the naphtha vapor may become unstable, and certain portions or components will readily crack to smaller molecules with concomitant carbon deposition. Stream 3 thus is preferably produced at a temperature ranging from 400° F. to 800°F.

Stream 4 consists of highly superheated steam, preheated usually to a temperature above 1500°F., and preferably to the range of 1500°F. to 1700°F. Although lower ratios

are feasible, it has been found that a range of molecules steam:carbon atom ratios between 3 to 1 and 6 to 1 is desirable in proportioning the relative flow rates of streams 4 and 3, in order to prevent accumulated deposition of carbon under normal operating conditions.

Stream 5 consists of air, preheated usually to a temperature above 800°F, and preferably to the range of 800°F to 1200°F. The proportion of air employed in the process is quite small, thus only enough air is used to provide a 3 to 1 molar ratio of hydrogen to nitrogen in the final ammonia synthesis gas. The streams 4 and 5 are preferably combined, to form a mixed steam-air stream 6 at a temperature of at least 1100°F. Stream 6 is now combined with naphtha vapor stream 3, and the mixed stream 7 is immediately passed into residence or gas conditioning chamber 8. It will be appreciated that streams 3, 4 and 5 may be separately passed into chamber 8, however premixing of the air and steam to form stream 6 is a preferable procedure since this results in better and more rapid mixing of the several streams. Thus, stream 3 is more rapidly dispersed and diluted due to the mixing with stream 6, prior to entry of the naphtha vapor into residence chamber 8. Consequently, the possibility of transient carbon formation or deposition due to cracking of the naphtha is reduced by the pre-mixing step.

In chamber 8, simultaneous reactions take place between and among the several reactants and intermediate components. The temperature of the process stream immediately rises, due to exothermic combustion of a portion of the naphtha with the oxygen content of the air. In addition, a portion of the naphtha is non-catalytically steam reformed due to the high temperature and high steam concentration in chamber 8. This endothermic reaction serves to produce free hydrogen, and also moderates the temperature rise due to combustion. A further portion of the naphtha is thermally cracked to lower hydrocarbons, due also to the high temperature level. However, simultaneous deposition and accumulation of free carbon does not instantaneously occur. Instead, the unstable lower unsaturated hydrocarbons are hydrogenated to a certain extent due to the in situ formation of hydrogen, which may possibly be formed in the nascent state. Thus, the resultant gaseous stream 9 contains significant proportions of steam, nitrogen, hydrogen, carbon dioxide, carbon monoxide, unsaturated hydrocarbons (mostly ethylene), methane and ethane. It should be understood, however, that these components are present on a transient or instantaneous basis. If stream 9 is allowed to reach stable equilibrium under these process conditions, significant formation and accumulated de-

position of free carbon will take place.

Under some conditions, the temperature in unit 8 may be in the range of 1450°F to 1500°F. However, with such low reaction temperatures, the formation of free carbon may readily occur, especially after all the residual free oxygen is consumed, unless the residence time is kept in the range of 0.05 to 0.33 seconds. With such short residence times, unreacted naphtha may pass into the following catalytic stage of the process, however, as will appear infra, the formation of free carbon is readily prevented in the catalytic stage by maintenance of a temperature level above 1600°F. In general, the residence time in chamber 8 must be kept below 1.0 seconds, and preferably in the range of 0.05 to 0.33 seconds, in order to achieve the desired reactions without carbon formation. In addition, the instantaneous mix temperature of stream 7 must be kept above 1000°F, since it has been found in practice that the various competing reactions will tend to form free carbon if the initial mix temperature is below 1000°F. This initial or instantaneous mixture temperature should preferably be in the range of 1400°F to 1700°F, in order to preclude carbon formation due to variation in process conditions. It will be evident that chamber 8 may actually, in terms of apparatus design, consist merely of an insulated pipe section extending between the point of mixing of the reactant streams and the entry of the conditioned gas stream into the catalyst bed section.

Stream 9 now passes into the catalytic reformer unit 10. Reformer 10 may be a unit of conventional design, such as shown in U. S. Patent 2,660,519. Thus, unit 10 is provided with a plurality of reformer tubes such as 11 having a bed or charge of reform catalyst 12, usually consisting of nickel or cobalt deposited on a suitable carrier. Tube 11 is externally heated by such means as combustion of fluid hydrocarbon streams 13 with air streams 14, with flue gas removal via 15.

As mentioned supra, it has been found that the temperature of the catalyst in bed 12 must generally be kept above 1600°F, in order to prevent carbon accumulation. An exception to this general requirement of 1600°F minimum temperature during catalytic reforming is the case where stream 9 contains unreacted free oxygen. Free oxygen could be present in stream 9 if residence time in unit 8 is kept very short. Under such circumstances, stream 9 and the initial portion of bed 12 in which free oxygen is present may be maintained at a lower temperature level, down to 1400°F, without concomitant accumulated deposition of free carbon. Of course, after all free oxygen is consumed, the catalyst bed must thereafter be kept at 1600°F or higher to prevent carbon deposition. As the process stream 9 passes into bed

12, endothermic steam reforming of hydrocarbons immediately takes place. In order to prevent a concomitant sudden drop in the in situ process temperature at the inlet end of bed 12 the equivalent linear velocity of the process stream in the bed 12 is maintained at 5 ft./second or above. "Equivalent" linear velocity refers to the gas velocity which would exist at normal operating conditions, if the tube were not filled with catalyst. It has been determined that this linear velocity should preferably be in the range of 10 ft./sec. to 30 ft./sec., in order to effectively spread out the reforming reaction through the bed 12 and thereby effectively prevent carbon deposition. Various other expedients may be adopted in this respect. Thus, the apparatus concept embodied in U. S. 2,801,159 may alternatively be employed in the present invention in order to more effectively disperse stream 9 into bed 12. For example, a perforated tube may be employed in the present invention in order to more effectively disperse stream 9 into bed 12. Other modifications e.g. diluting the upper portion of catalyst bed 12 with inert material such as porcelain, so as to reduce the amount of hydrocarbon reformed per unit volume of catalyst, may also be adapted in order to extend the reforming reactions through bed 12 and thereby prevent localized temperature decrease and concomitant carbon deposition.

The resultant reformed gas stream is removed from tube 11 via 16. Stream 16 contains essentially only hydrogen, nitrogen, carbon monoxide, carbon dioxide and steam. A typical volume analysis of stream 16 (Table I infra, run #12) was as follows: 51.4% hydrogen, 22.5% nitrogen, 13.0% carbon dioxide, 12.1% carbon monoxide, 1.0% methane and 0.0% unsaturated hydrocarbons. This analysis was on a dry basis, the total product stream generally contained about 50% steam on a total volume basis. In order to produce a finished ammonia synthesis gas with a 3:1 ratio of hydrogen to nitrogen, stream 16 is now processed by conventional technology, not shown. This will include the usual process steps of CO-oxidation, carbon dioxide removal, etc. It will be understood that the process of the present invention may be carried out with other proportions of air, besides that which will yield a final 3:1 ratio of hydrogen to nitrogen. In some cases, such as when stream 16 is to be employed as a reducing gas, the proportion of air will not necessarily be exactly such as to yield a final 3:1 ratio. Somewhat more air may be employed in such cases, since a higher proportion of nitrogen in the final product gas will not be objectionable. Using relatively more air in the process of the present invention is advantageous since lower preheat temperatures

- are required and further since the possibility of carbon deposition due to process upsets is lessened. Depending on the purity and carbon forming tendency of the particular naphtha, it will also be possible in some cases to decrease the ratio of air employed in the process without depositing carbon in the catalyst bed. In this case, equipment size is reduced and a richer gas is produced.
- If the product gas is to be employed in ammonia synthesis, further nitrogen may be added at a later stage of the process, preferably after carbon dioxide removal.
- It has been found that operating pressure does not appear to be a significant variable in the process of the present invention. Although pressure is not critical, an operating pressure in the range of 100 psig to 300 psig is preferable since reform plant equipment size is reduced, and also because subsequent compression costs are reduced. In addition, reforming at elevated pressure yields a high pressure process gas which thus may be directly treated for carbon dioxide removal by hot potassium carbonate scrubbing.
- It will be evident to those skilled in the art that the significant process variables in steam reforming of naphtha according to the present invention are closely inter-related. Thus, the required minimum preheat temperatures of the reactant streams prior to chamber 8 will depend principally on the residence time in 8 prior to entry of the mixed stream via 9 into bed 12. With lower residence times in the range of 0.05 to 0.10 seconds, it has been found that the process may be successfully carried out with a residence chamber temperature in the range of 1450°F to 1500°F. However, if a longer residence interval up to 1.0 seconds is required, then the initial streams 3, 4 and 5 must be preheated to higher levels so as to provide a temperature range of 1650°F to 1690°F in chamber 8, in order to prevent accumulated deposition of free carbon in actual operation of the process.
- Similarly, it will be recognized that a minimum steam/carbon ratio of 3:1 is generally required, in order to satisfy material balance considerations by providing sufficient steam for complete reaction with the naphtha. However, a steam/carbon ratio in the range of 5:1 to 7:1 has been found to be optimum in providing complete reaction, satisfactory reaction rate, and minimum tendency for carbon formation due to process upsets. Higher proportions of process air will generally be required if minimum steam/carbon ratios are adopted, in order to prevent carbon deposition.
- Following are tabulations of various pilot plant runs, which formed the basis for establishing the critical aspects and ranges which are the novel features of the present invention. Table I provides typical optimum conditions for essentially carbon-free operation, while Table II is a tabulation of various runs in which carbon formation and accumulated deposition was a significant factor. A thin coating of carbon was found on the catalyst in many of the runs in Table I, however, this coating did not result in any accumulated deposition or buildup of free carbon on the catalyst. Apparently the steam-carbon reaction rate in these runs was equal to or faster than the carbon formation rate. In any case, it was found that process equilibrium was attained without accumulated deposition of carbon. Thus runs #5 and #6 in Table I infra were carried out under substantially identical conditions. Run #5 was of 49 hours duration while run #6 was extended to 269 hours duration. Analysis showed no accumulation of carbon in the catalyst after run #6, as compared to the catalyst after run #5.

TABLE I.  
CATALYTIC STEAM REFORMING OF PETROLEUM NAPHTHA—OPTIMUM CONDITIONS\*

Run No.	Feed Rates			Inlet Pressure (PSIG)	Residence Time (seconds)	Reforming Temp. (°F)		Linear Velocity ft./sec.
	Naphtha (G.P.H.)	Steam (SCFH)	Air (SCFH)			In.	Out	
1.	0.15	150	23	15	0.028	1400	1600—1650	17—19
2.	0.21	500	30	75	0.05	1400—1500	1600—1650	16—17
3.	0.44	380	60	75	0.033	1440—1480	1630	15
4.	0.44	375	60	75	0.13	1400—1500	1600—1650	15
5.	0.92	700	120	150	0.03	1430—1490	1600—1640	15

\* Negligible or slight carbon formation.

TABLE I—*cont.*

## CATALYTIC STEAM REFORMING OF PETROLEUM NAPHTHA—OPTIMUM CONDITIONS\*

5	Run No.	Feed Rates			Inlet Pressure (PSIG)	Residence Time (seconds)	Reforming Temp. (°F)		Linear Velocity ft./sec.
		Naphtha (G.P.H.)	Steam (SCFH)	Air (SCFH)			In	Out	
10	6.	0.92	700	120	150	0.03	1430— 1500	1600— 1650	15
	7.	0.92	700	120	150	0.24	1600— 1650	1625— 1650	15
	8.	0.92	700	120	150	0.24	1630	1650	15
15	9.	1.2	1000	150	250	0.32	1575— 1630	1630— 1650	13
	10.	0.92	700	130	150	0.27	1610— 1670	1650— 1670	15
	11.	0.72	700	110	150	0.27	1600— 1615	1650— 1660	15
20	12.	1.2	1000	155	150	0.30	1640	1605	15
	13.	1.15	1000	155	150	0.33	1650— 1665	1700— 1775	5.6
25	14.	1.15	1000	155	150	0.33	1640— 1620	1600	15

\* Negligible or slight carbon formation.

TABLE II.

## CATALYTIC STEAM REFORMING OF PETROLEUM NAPHTHA—MISCELLANEOUS RUNS\*

30	Run No.	Feed Rates			Inlet Pressure (PSIG)	Residence Time (seconds)	Reforming Temp. (°F)		Linear Velocity ft./sec.
		Naphtha (G.P.H.)	Steam (SCFH)	Air (SCFH)			In	Out	
35	1.	0.40	380	60	75	0.033	1310	1600— 1650	15
	2.	0.40	200	60	75	0.05	1400	1650	9.5
	3.	0.40	200	60	75	0.06	800— 900	1600— 1650	9.5
	4.	0.70	585	115	75	0.02	1330	1620	22
40	5.	0.24	500	45	75	0.031	1400	1650	16
45	6.	0.40	400	60	76	0.033	1400— 1450	1600— 1650	15
	7.	0.70	585	120	75	0.023	1400— 1450	1600— 1650	22
	8.	0.92	700	130	150	0.033	1500	1650	15
	9.	1.1	850	140	75	0.015	1410	1630	32
	10.	0.62	500	90	150	0.05	1400— 1500	1600— 1650	10
	11.	0.92	700	120	150	0.13	1450	1620	15

50 \* Moderate or heavy carbon formation.

TABLE II—cont.

CATALYTIC STEAM REFORMING OF PETROLBUM NAPHTHA—MISCELLANEOUS RUNS*									
5	Run No.	Feed Rates			Inlet Pressure (PSIG)	Residence Time (seconds)	Reforming Temp. (°F)		Linear Velocity ft./sec.
		Naphtha (G.P.H.)	Steam (SCFH)	Air (SCFH)			In	Out	
	12.	0.31	250	50	150	0.30	1450—1500	1640	5
10	13.	0.24	200	20	75	0.18	1450—1500	1650	7.5
	14.	0.92	700	120	150	0.24	1460	1630	15
	15.	0.92	700	120	150	0.30	900—1000	1650	12
15	16.	1.1	900	140	150	0.35	950	1600—1640	14
	17.	0.92	700	125	150	0.27	1540—1600	1450—1500	14.5
	18.	0.92	710	125	150	0.03	1320—1340	1450—1480	14.5
20	19.	1.15	1000	155	150	0.33	1600—1615	1600	5.6
	20.	1.15	1000	155	150	0.33	1570—1575	1630—1700	5.6
25	21.	1.15	1000	155	150	0.33	1630	1650—1700	5.6
	22.	1.15	1000	155	150	0.33	1630—1640	1600	15
	23.	1.15	1000	155	150	0.33	1605	1600	15
30	24.	1.15	1000	155	150	0.33	1605	1550	15

\*Moderate or heavy carbon formation.

Following are analyses of the two commercial naphthas employed in the above runs. All runs employed naphtha "A", except for run #12 of Table 1 in which naphtha "B" was tested. It is evident from the fact that naphtha "B" was also success- 40

fully reformed, that naphthas of varying compositions and analyses may be successfully reformed by suitable selection of process variables within the scope of the present invention.

TABLE III.

SPECIFICATION OF TESTED NAPHTHAS						
45	Naphtha Type	...	...	...	A	B
	Initial Boiling Point (°F)	...	...	...	114—120	130
	End Point (°F)	...	...	...	229—248	242
	Specific Gravity @ 60°F	...	...	...	0.66	0.7047
	Composition (wt. %)					
50	Paraffins	...	...	...	92.4—93.0	57.4
	Naphthenes	...	...	...	6.2—7.5	32.5
	Aromatics	...	...	...	0.1—1.1	9.4
	Olefins	...	...	...	0.1—0.2	0.7
	Sulfur Content (ppm)	...	...	...	11—27	9



The test equipment was modified in order to withdraw a test sample of the gas in the residence chamber. In this case, the operating conditions of run #7 of Table I were employed, with the gas sample being withdrawn at 0.20 seconds residence time and quenched. Inlet temperatures of the reactant streams to the residence chamber were as follows:

10	Steam:	1675—1680°F
	Air:	940—1000°F
	Naphtha:	600—700°F

Analysis of the residence chamber gas (dry basis) @ 0.20 seconds residence time was as follows (volume %):

		Sample #1	Sample #2
	Carbon dioxide ... ..	7.0	7.5
	Carbon monoxide ... ..	7.0	8.9
20	*Unsaturated hydrocarbons	14.1	10.9
	Methane ... ..	7.0	8.7
	Ethane ... ..	5.0	3.0
	Hydrogen ... ..	13.9	15.5
	Nitrogen ... ..	46	45
25	*mostly ethylene		
	% of Naphtha gasified ...	95	97
	Adiabatic temp. (°F) ...	1690	1730

At a lower inlet steam temperature of 1600°F, the adiabatic temperature at 0.20 seconds residence time was in the range of 1630—1690°F.

From the above analyses of the gas stream in the residence chamber, certain conclusions may be reached with respect to probable reaction mechanism. Thus, since no oxygen is present, combustion of naphtha has already taken place to completion at 0.20 seconds. Since some unsaturated hydrocarbons as well as ethane and methane are present, it is evident that some thermal cracking of naphtha also took place, probably together with some hydrogenation of unstable free radicals and unsaturated carbon linkages. This thermal cracking thus was accomplished without carbon accumulation. Finally some free hydrogen is also present hence non-catalytic (thermal) steam reform of naphtha also took place.

Thus, the competing reactions of naphtha combustion, cracking and steam reform are carried out in the first stage of the process of the present invention. It has been determined that, by maintenance of reaction conditions within certain critical ranges, these competing reactions may be carried out without carbon accumulation. In addition, the resulting unstable process stream, when passed to catalytic steam reforming before further reaction ensues, is successfully steam

reformed to yield further hydrogen and carbon monoxide in a second stage without carbon accumulation. In summary, the present invention essentially accomplishes the steam reforming of naphtha by a process which partially gasifies the naphtha vapor using preheated air and steam. It has been determined that the resulting mixed gas stream may be successfully converted to a synthesis gas by conventional endothermic catalytic steam reforming without accumulated deposition of carbon, if the mixed gas stream is passed into contact with a catalyst bed before final process equilibrium is reached. Thus, as discussed supra, the critical features of the present invention essentially involve the maintenance of the several inter-related process variables within operating limits in which the new result of the present invention is achieved, namely the continuous steam reforming of naphtha. As indicated supra, the process of the present invention may be employed to produce a reducing gas or other product gas stream with varying proportions of hydrogen and nitrogen, by varying the initial proportion of air. The lower limit of air employable will depend, in any specific instance, on the carbon forming tendency of the particular naphtha to be reformed and thus will be empirically determined in practice.

#### WHAT WE CLAIM IS:—

1. A process for forming a hydrogen-nitrogen gas stream which comprises vaporizing and preheating naphtha to a temperature up to 1000°F., superheating steam, and preheating air, combining said streams of naphtha, steam and air to form a mixed gaseous stream at a temperature of at least 1000°F., reacting said mixture for an interval less than 1.0 seconds in which said naphtha is simultaneously oxidized, cracked and partially reformed without accumulated deposition of free carbon, and catalytically reforming the resulting gas mixture in contact with a reform catalyst at an equivalent linear velocity of at least 5 ft./sec., said catalyst being externally heated to maintain a reaction temperature of at least 1400°F., whereby a final reformed gas mixture substantially free of hydrocarbons and comprising hydrogen, nitrogen, steam, carbon monoxide and carbon dioxide is produced, without accumulated deposition of free carbon.

2. A process according to claim 1, in which the naphtha is vaporized and preheated to a temperature of 400°F. to 800°F., the mixed gaseous stream of naphtha, steam and air is at a temperature of 1400°F. to 1700°F. and pressure in the range of 100 to 300 psig, and said mixed gaseous stream has a molecules of steam/atoms of carbon ratio between 5 to 1 and 7 to 1, and is reacted for a time interval from 0.05 to 0.33

seconds, and the resulting gas mixture catalytically reformed with the catalyst maintained at a reaction temperature of at least 1600°F., said gas mixture having a linear gas velocity in the range of 10 to 30 ft./sec. during said catalytic reform.

3. A process according to claim 2, in which the mixed gas stream produced after said reaction time interval is divided into a plurality of partial streams and said partial streams are passed into contact with said catalyst in a catalyst bed at a plurality of spaced intervals, whereby the resulting catalyst reforming reaction takes place at a substantially uniform rate throughout said catalyst bed and localized temperature depression is prevented.

4. A process according to either of claims 2 and 3, in which said catalyst is disposed in a bed having progressively increasing catalytic activity per unit volume of bed in the downstream direction of gas flow.

5. A process according to claim 4, in

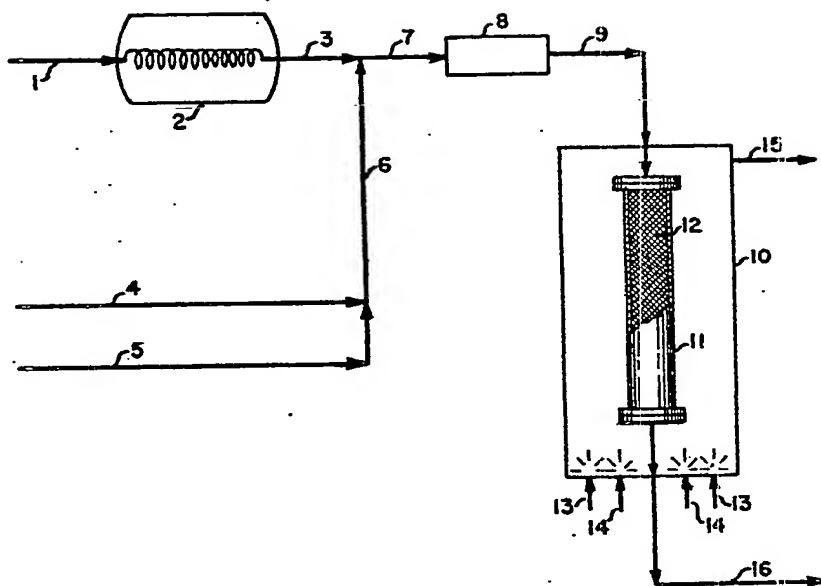
which said bed is vertically oriented and said mixed gas stream is passed downwards through the bed.

6. A process according to any one of the preceding claims, in which said streams of naphtha, steam and air are combined by first mixing together the steam and air to form a first mixed stream at a temperature of at least 1100°F., and thereafter combining said first mixed stream with the vaporized naphtha.

7. A process as claimed in claim 1 for forming a hydrogen-nitrogen gas stream substantially as hereinbefore described in the Examples.

8. A hydrogen-nitrogen gas stream when produced by a process according to any one of claims 1 to 7.

STEVENS, LANGNER, PARRY  
& ROLLINSON,  
Chartered Patent Agents,  
Agents for the Applicants.



**THIS PAGE BLANK (USPTO)**